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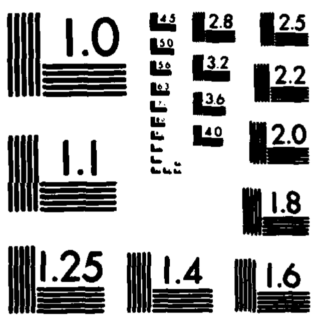

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Contract N00014-80-C-0472

Task No. NR 056-749

TECHNICAL REPORT No. 45

Laser-Induced Surface Migration via Surface Plasmons

by

William C. Murphy, Xi-Yi Huang and Thomas F. George

Prepared for Publication

in

Chemical Physics Letters

Department of Chemistry
University of Rochester
Rochester, New York 14627

December 1983

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE

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1. REPORT NUMBER: UROCHESTER/DC/83/TR-45	2. GOVT ACCESSION NO.
3. RECIPIENT'S CATALOG NUMBER	
4. TITLE (and Subtitle): Laser-Induced Surface Migration via Surface Plasmons	5. TYPE OF REPORT & PERIOD COVERED
	6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s): William C. Murphy, Xi-Yi Huang and Thomas F. George	8. CONTRACT OR GRANT NUMBER(s): N00014-80-C-0472
9. PERFORMING ORGANIZATION NAME AND ADDRESS: Department of Chemistry, University of Rochester, Rochester, New York 14627	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS: NR 056-749
11. CONTROLLING OFFICE NAME AND ADDRESS: Office of Naval Research, Chemistry Program Code 472, Arlington, Virginia 22217	12. REPORT DATE: December 1983
	13. NUMBER OF PAGES: 7
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)	15. SECURITY CLASS. (of this report): Unclassified
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

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17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

Prepared for publication in Chemical Physics Letters

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

SURFACE MIGRATION	CO_2 LASER
LASER-INDUCED	OXYGEN ION ON ALUMINUM
SURFACE PLASMONS	61.3 MICRONS PER SECOND
CLASSICAL MODEL	FIVE ORDERS OF MAGNITUDE ENHANCEMENT

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

A classical model coupling a charged adspecies to a laser-induced surface plasmon is presented. Such coupling can enhance the rate and specify the direction of surface migration. For the particular case of an atomic oxygen ion of charge -1 adsorbed on aluminum which is exposed to CO_2 laser radiation of intensity of 1 W/cm^2, the velocity of migration (61.3 microns/sec) is five orders of magnitude greater than the usual thermal velocities observed at room temperature.

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Chemical Physics Letters, in press

LASER-INDUCED SURFACE MIGRATION VIA SURFACE PLASMONS

William C. Murphy, Xi-Yi Huang* and Thomas F. George

Department of Chemistry
University of Rochester
Rochester, New York 14627

A classical model coupling a charged adspecies to a laser-induced surface plasmon is presented. Such coupling can enhance the rate and specify the direction of surface migration. For the particular case of an atomic oxygen ion of charge -1 adsorbed on aluminum which is exposed to CO_2 laser radiation of intensity 1 W/cm^2, the velocity of migration (61.3 μm/sec) is five orders of magnitude greater than the usual thermal velocities observed at room temperature.

* Permanent address: Institute of Physics, Academia Sinica, Beijing (Peking), The People's Republic of China

A

Migration of adsorbed particles on a solid surface is an important process in catalytic reactions.[1-5] Such motion has been observed even for adsorbates with very high binding energies at relatively low temperatures.[1] This surface migration is essentially random motion that proceeds at a typical adsorbate velocity of a few angstroms per second.[1,2]

Adsorbed particles on a surface, however, can be strongly influenced by the existence of surface plasmons. For example, it has been theoretically argued that the interaction between adspecies can be enhanced by these surface waves.[6] Furthermore, laser-induced periodic surface structure has been explained in terms of surface plasmons.[7] In the following, we shall examine the effect that a surface plasmon can have on the motion of a charged adspecies at low temperatures. We shall discuss the possibility of using a laser-excited surface plasmon to control both the rate and direction of surface migration.

If a smooth metal surface is exposed to laser radiation of an appropriate frequency, a surface plasmon can be excited via frustrated reflection.[8] This plasmon will have an electric field, $\vec{E}$, associated with it above the surface of the form[9]

$$\frac{\vec{E}}{E_0} = \left(\frac{k_x}{k_g}, 0, -\frac{k_z}{k_g}\right) \exp[i(k_x x + k_z z - \omega t)] + \text{c.c.}, \tag{1}$$

where the z-direction is perpendicular to the surface, x is parallel and in the direction of the plasmon propagation, and E_0 is the amplitude and ω the frequency of the laser field. The wavenumber k_g for the laser in the gas medium above the metal and k_x and k_z for the surface plasmon are given by

$$k_g = \frac{\omega}{c} \tag{2}$$

$$k_x = \frac{\omega}{c}\sqrt{\frac{\varepsilon(\omega)}{\varepsilon(\omega)+1}} \tag{3}$$

$$k_z = \frac{\omega}{c}\frac{1}{\sqrt{\varepsilon(\omega)+1}} \quad , \tag{4}$$

where c is the speed of light.

The dielectric function of the metal, $\varepsilon(\omega)$, will in general be less than negative one for the plasmons excited. Under this condition, the x-component of the wavevector, Eq. (3), will be real and the z-component, Eq. (4), will be imaginary:

$$k_z \equiv i\kappa \ . \tag{5}$$

If a particle of charge q is now introduced above the surface, it will couple to the plasmon electric field. The equations of motion for this particle can be readily obtained from Eq. (1) as

$$m\ddot{x} = \frac{2q\kappa E_0}{k_g} \sin(k_x x-\omega t)e^{-\kappa z} - \frac{\partial V(x,y,z)}{\partial x} \quad , \tag{6a}$$

$$m\ddot{z} = \frac{2qk_x E_0}{k_g} \cos(k_x x-\omega t)e^{-\kappa z} - \frac{\partial V(x,y,z)}{\partial z} \quad , \tag{6b}$$

where m is the mass of the adspecies and V(x,y,z) is the interaction potential between the adspecies and the surface. This interaction can be quite complicated,[10,11] especially in the presence of the surface plasmon. We shall assume that the interaction is sufficiently strong to confine the charged particle to an equilibrium distance from the surface, $z = z_{eq}$. However, it will be free to move along the plane of the surface. These conditions would be characteristic of a physisorbed state.

Under these assumptions, Eq. (6a) can be simplified and converted to and integral form,

$$x(t) = \omega^2 C\int_0^t dt'\int_0^{t'} dt'' \sin[k_x x(t'') - \omega t''], \tag{7}$$

where the constant is

$$C \equiv \frac{2q\kappa E_0 e^{-\kappa z_{eq}}}{m\, k_q\, \omega^2} . \tag{8}$$

We now change the variable of integration in Eq. (7) to

$$u'' = k_x x(t'') - \omega t'' \tag{9}$$

and similarly for t'. Furthermore, we note that the velocity of the particle will be much slower than the plasmon:

$$\dot{x}(t'') << \frac{\omega}{k_x} . \tag{10}$$

Under these conditions, we can readily integrate Eq. (7) to give

$$x(t) = C\{k_x x(t) - \omega t - \sin[k_x x(t) - \omega t]\}. \tag{11}$$

However, for any time greater than a few periods of the laser frequency, the oscillatory term will be insignificant. Therefore,

$$x(t) = \frac{C\omega}{k_x C - 1}\, t. \tag{12}$$

Consequently, coupling a charged adspecies to the plasmon will produce a linear motion parallel to the plasmon.

If an aluminum surface is exposed to a laser of low intensity (1 W/cm^2) with a frequency of 1.8×10^{14}Hz (CO_2 laser at 10.6 μm), surface plasmons can be excited. We now consider an atomic oxygen ion of charge -1 adsorbed on the surface, which will couple to this plasmon. The resultant velocity can be obtained from Eqs. (8) and (12) as

$$\dot{x} = 61.3\ \mu m/sec. \tag{13}$$

This is substantially larger than the usually thermal velocities of a few angstroms per second that are observed at room temperature. Furthermore, we can easily increase this speed by using a laser of higher intensity. It should also be noted that the velocity of a *negatively charged particle* is with the plasmon; the positive particle will move against it. Thus, the plasmon-induced motion has a <u>preferred</u> <u>direction</u>.

We have shown that a laser-excited surface plasmon can impart substantial motion to a charged adspecies. However, we have only considered this effect *for weakly-bound* adsorbates at low temperatures. The exact form of the surface interaction potential was not considered, and the phenomena of surface relaxation that often accompanies migration[2,12] was not examined. Finally, it should be noted that the interplay of the surface plasmon with the adspecies/surface potential could have a substantial effect on surface migration. Research to overcome these limitations in this model is now in progress.

Acknowledgments

This research was supported in part by the Office of Naval Research, the Air Force Office of Scientific Research (AFCS), United States Air Force, under Grant AFOSR-82-0046, and the U.S. Army Research Office. The United States Government is authorized to reproduce and distribute reprints for governmental purposes notwithstanding any copyright notation hereon. TFG acknowledges the Camille and Henry Dreyfus Foundation for a Teacher-Scholar Award (1975-84) and the John Simon Guggenheim Foundation for a Fellowship (1983-84).

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